Electrochemistry

Where it helps?

- **Electrochemistry** is the study of chemical reactions involving electricity and electric current, discharge, electric charge, charged particles, electrochemical series, electrolysis, ions, nucleus, potential difference, , voltaic cells , corrosion …etc.
- All these points are of great value in industry during designing or providing some controlling switches.

Where Electrochemistry is used?

Electricity **Chemistry**

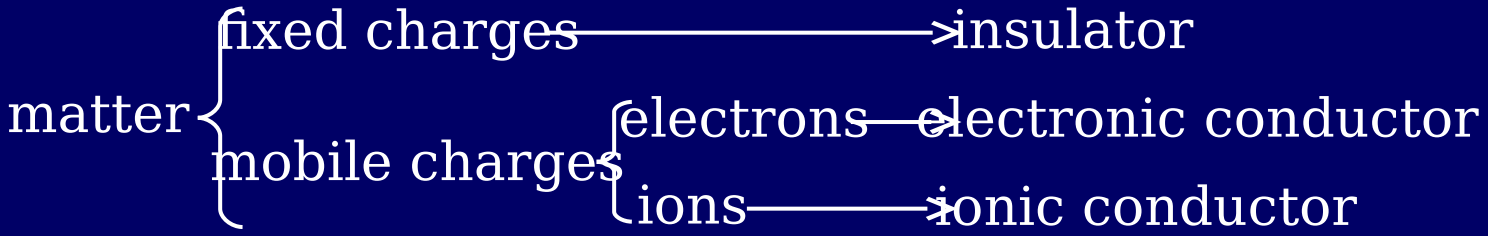
Electro-chemistry

Physics

Material Science

Mathematics

Types of conductors



matter

fixed charges → insulator

mobile charges

electrons → electronic conductor

ions → ionic conductor

electronic conductors	ionic conductors	mixed
metals	seawater [Na^+(aq), SO_4^{2-}(aq), etc]	plasmas
graphite	ZrO_2(s) [O^{2-}]	$e^-(NH_3) + Na^+(NH_3)$
semiconductors	$RbAg_4I_5$ [Ag^+]	H_2 in Pd [$H^+ + e^-$]
PbO_2	pure water [H_3O^+(aq), OH^-(aq)]	

ELECTROLYTIC CONDUCTION RESISTIVITY AND CONDUCTIVITY

- The resistance, *R,* of any electrical conductor is proportional to its length, [*l*], and inversely proportional to its cross-sectional area, [a]

$$R \propto \frac{l}{a}$$

- It is therefore possible to write

$$R = \frac{\rho l}{a}$$

  in which [ρ] is proportionality constant known as the *resistivity* of the conductor

  As [*R*] is a resistance, [*l*]is a length and [a] is an area it can be seen from equation that [ρ] must have the units of (resistance) (length). For example, a piece of copper of length 0.2 m and cross-sectional area 10^{-4} m^2 has a resistance of $3.45 \times 10^{-5}\Omega$.

- Substituting in the equation
  the resistivity of copper is given by:

$$\rho = \frac{Ra}{l}$$

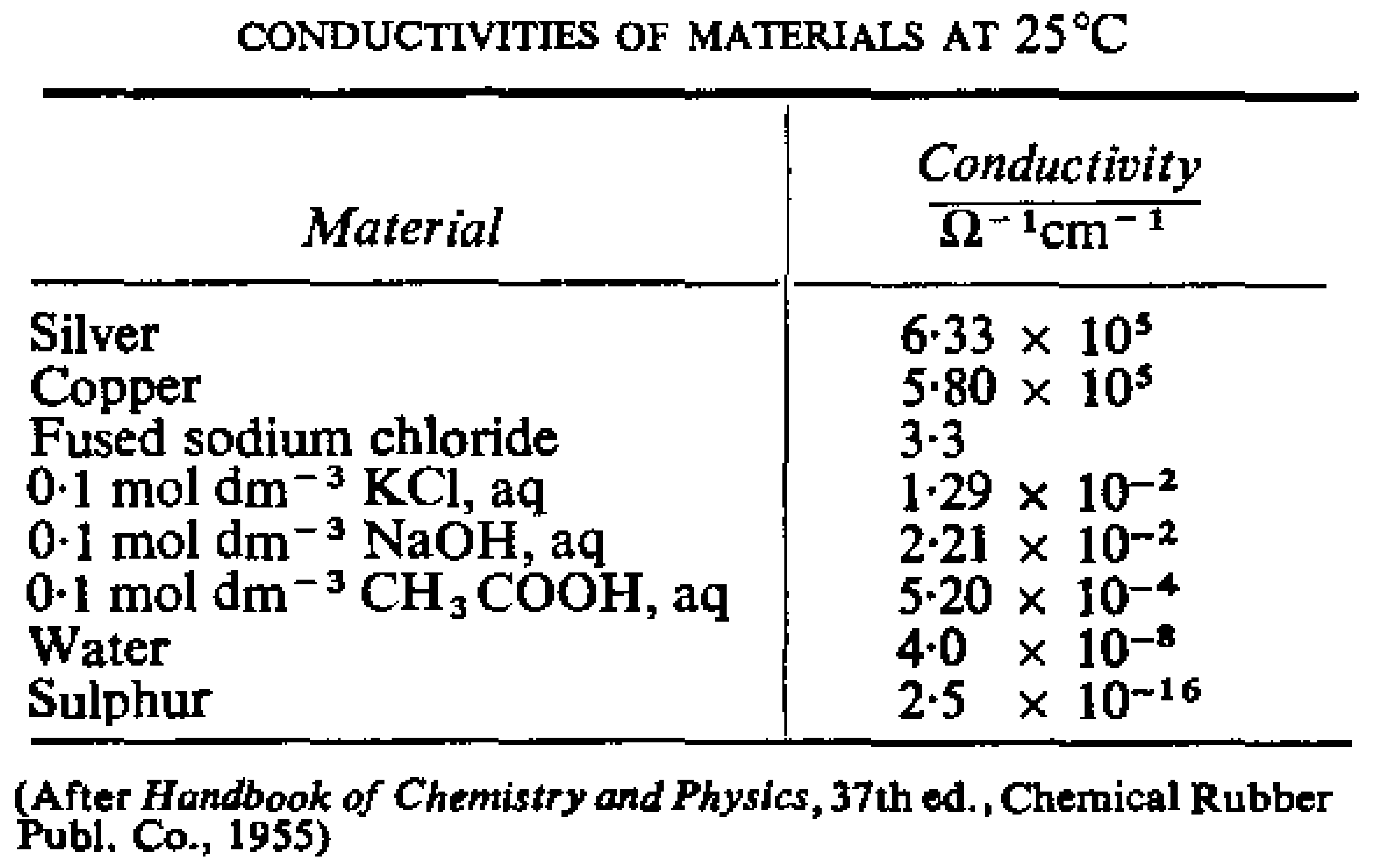
$$\rho = \frac{3{\cdot}45 \times 10^{-5}\,\Omega \times 10^{-4}\,\mathrm{m}^2}{0{\cdot}2\,\mathrm{m}}$$

or

$$\rho = 1{\cdot}725 \times 10^{-8}\,\Omega\,\mathrm{m}$$

In electrolytic conduction we are more concerned with conductance than resistance, and as a material is a better conductor the lower its resistance, conductance is related in a reciprocal fashion to resistance. We therefore define conductivity κ as the reciprocal of resistivity

$$\kappa = \frac{1}{\rho}$$



CONDUCTIVITIES OF MATERIALS AT 25°C

Material	*Conductivity* / $\Omega^{-1}\text{cm}^{-1}$
Silver	$6{\cdot}33 \times 10^{5}$
Copper	$5{\cdot}80 \times 10^{5}$
Fused sodium chloride	$3{\cdot}3$
$0{\cdot}1$ mol dm^{-3} KCl, aq	$1{\cdot}29 \times 10^{-2}$
$0{\cdot}1$ mol dm^{-3} NaOH, aq	$2{\cdot}21 \times 10^{-2}$
$0{\cdot}1$ mol dm^{-3} CH_3COOH, aq	$5{\cdot}20 \times 10^{-4}$
Water	$4{\cdot}0 \times 10^{-8}$
Sulphur	$2{\cdot}5 \times 10^{-16}$

(After *Handbook of Chemistry and Physics*, 37th ed., Chemical Rubber Publ. Co., 1955)

$$\kappa = \frac{l}{Ra}$$

$$\text{According to Ohm's law} \quad R = \frac{V}{I}$$

$$\text{and hence} \quad \kappa = \frac{Il}{Va}$$

$$\text{which can be reaaranged to give:}$$

$$\kappa = \frac{I/a}{V/l} = \frac{\text{current density}}{\text{Potential drop per lengt}}$$

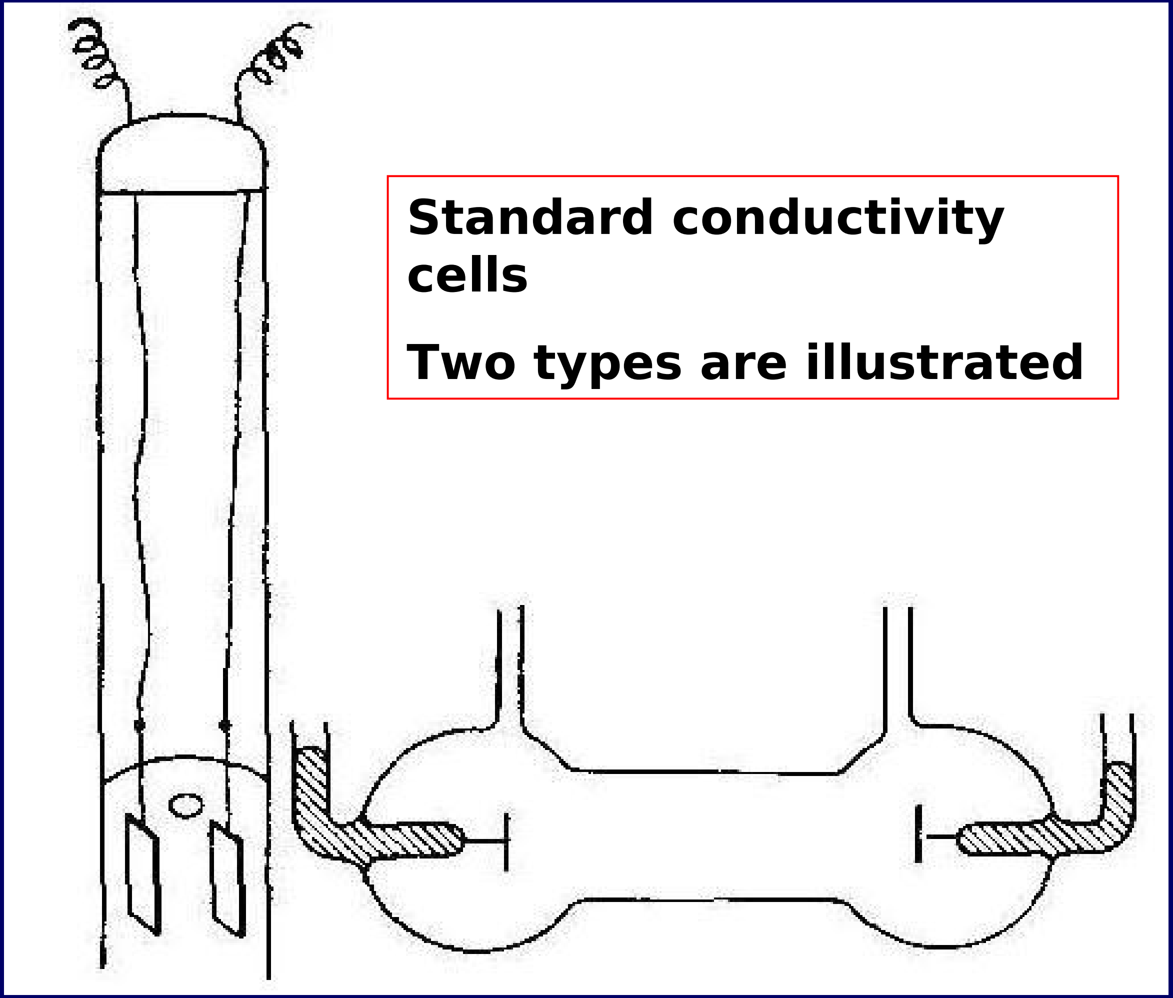
- ***I/a*** is the current per unit cross-sectional area. This is known as the current density and represented by the symbol *j*. *U/l* s the potential fall per unit length which is known as the potential gradient or electric field intensity, ***E.*** Thus conductivity may be regarded as the current passing across unit area under unit potential gradient

$$\kappa = \frac{j}{E}$$

MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES

- In measuring the conductance of an electrolyte, the property which is actually determined is the resistance, the conductivity being the reciprocal of resistance

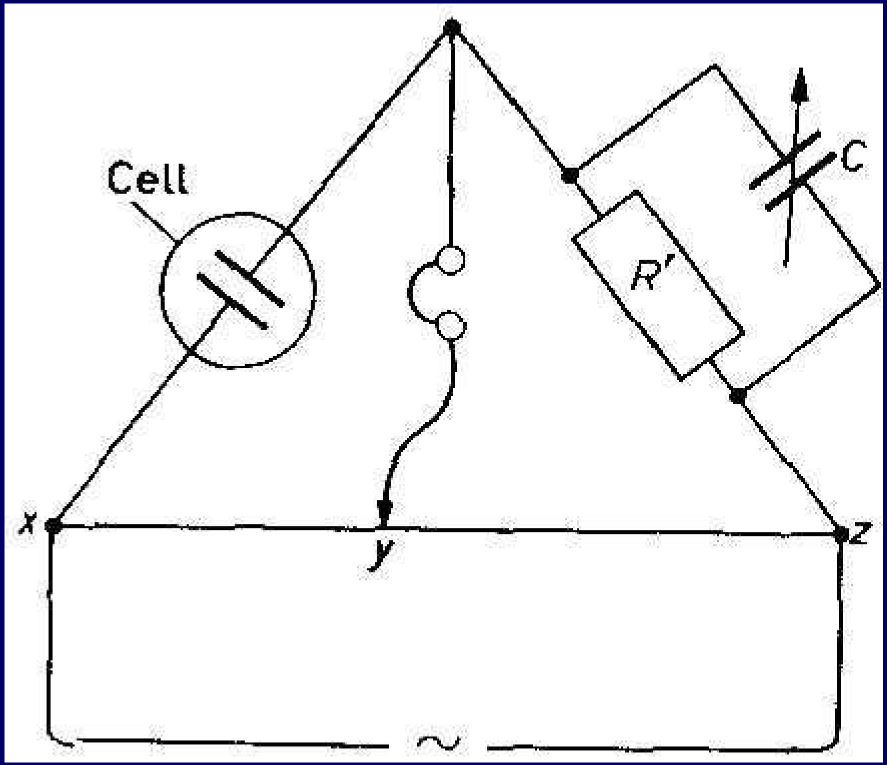
Measurement of conductance



Standard conductivity cells

Two types are illustrated

- The electrolyte solution is accommodated in a *conductance cell* which comprises one arm of a Wheatstone bridge circuit. Two examples of conductance cells are shown in the previous *Figure.* They usually consist of glass vessels containing two electrodes a fixed distance apart and it is the resistance of that volume of solution contained between the electrodes which is measured. When the resistance of a weakly conducting solution is to be determined, it is preferable to have electrodes of large cross-sectional area separated by only a small distance. This will reduce the resistance of the electrolyte contained between the electrodes to a value which is conducive to easy measurement . With a more strongly conducting solution the electrodes may be smaller and farther apart.



Whealstone Bridge circuit

If the balance point is at y, as shown in *Figure* , then the resistance, [**R**] of the cell is obtained from the expression

$$\frac{R}{R'} = \frac{xy}{yz}$$

ONLY AC CURRENT IS USED

WHY?

MOLAR CONDUCTIVITY

- The conductivities of electrolytes vary greatly with concentration. Comparison of the conductances of different electrolytes is more useful when some account is taken of concentration and for this reason a new term is defined.
- *Molar conductivity,* Λ, is defined by
  $\Lambda = \kappa/C$ C= concentration
- The basic units of molar conductivity are Ω^{-1} m^2 mol^{-1} but units of the type Ω^{-1} cm^2 mol^{-1} are equally accepted .

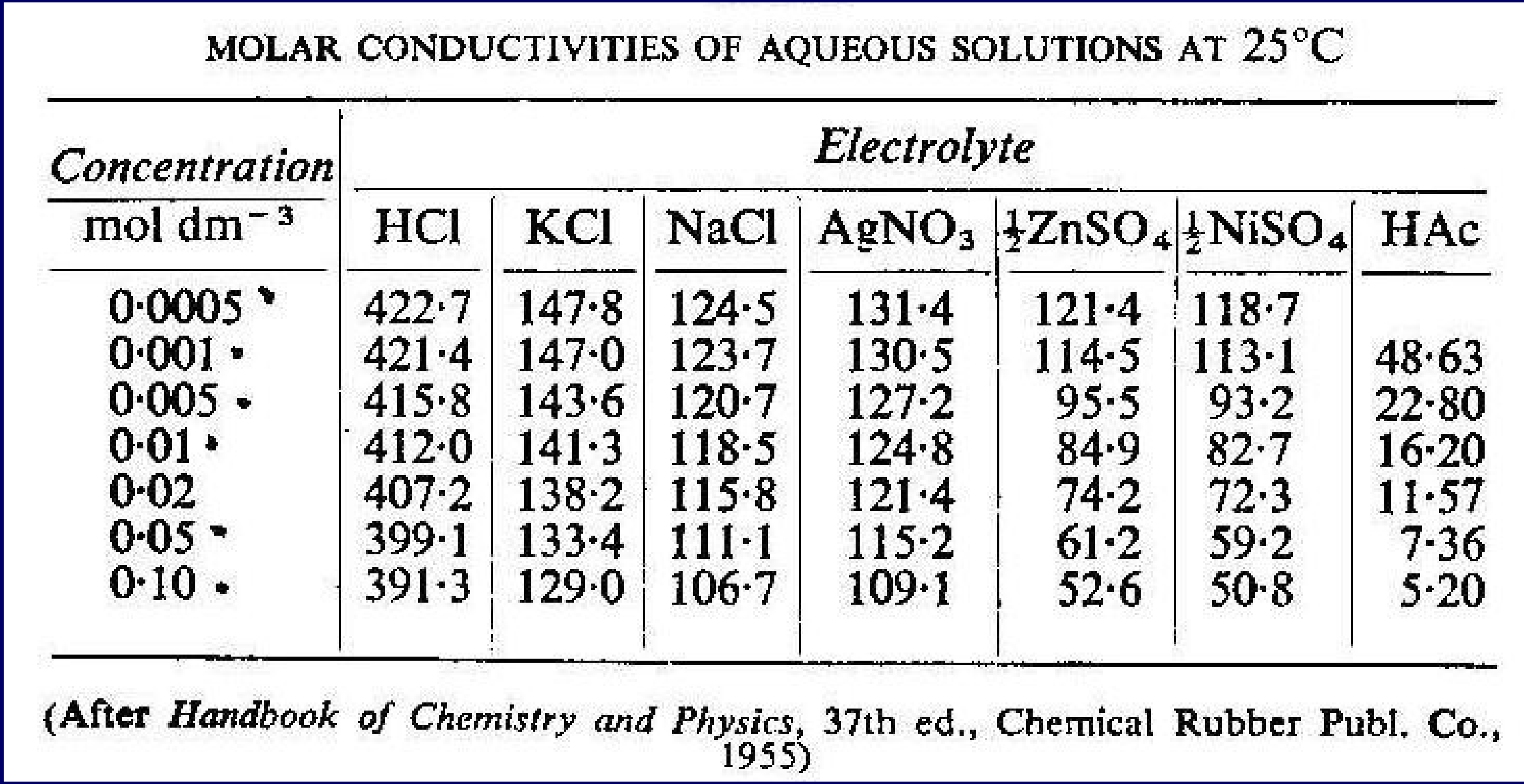
- The conductivity of potassium chloride solution at a concentration of 10^{2} mol m^{-3} is I.29 Ω-1 rn^{-1} at 25°C. The molar conductivity of this solution is thus given by

$$\Lambda = \frac{1{\cdot}29\ \Omega^{-1}\ \mathrm{m}^{-1}}{10^{2}\ \mathrm{mol\ m}^{-3}}$$

$$= 1{\cdot}29 \times 10^{-2}\ \Omega^{-1}\ \mathrm{m}^{2}\ \mathrm{mol}^{-1}$$

- In the comparison of the molar conductivities can yield a lot of information but to do so we need to compare molar conductivities where the various amounts of substances comprising a mole carry the ***same*** number of charges.
- For example, in the comparison of the molar conductivities of sodium chloride and zinc sulphate it is better to specify ***a mole*** of sodium chloride as NaC1 and to specify ***a mole*** of zinc sulphate as ½ $ZnSO_4$. If the moles of sodium chloride and zinc sulphate are specified in this way, ***a mole of each provides the same number of charges and the molar conductivities of each will be more comparable.***

VARIATION OF MOLAR CONDUCTIVITY WITH CONCENTRATION

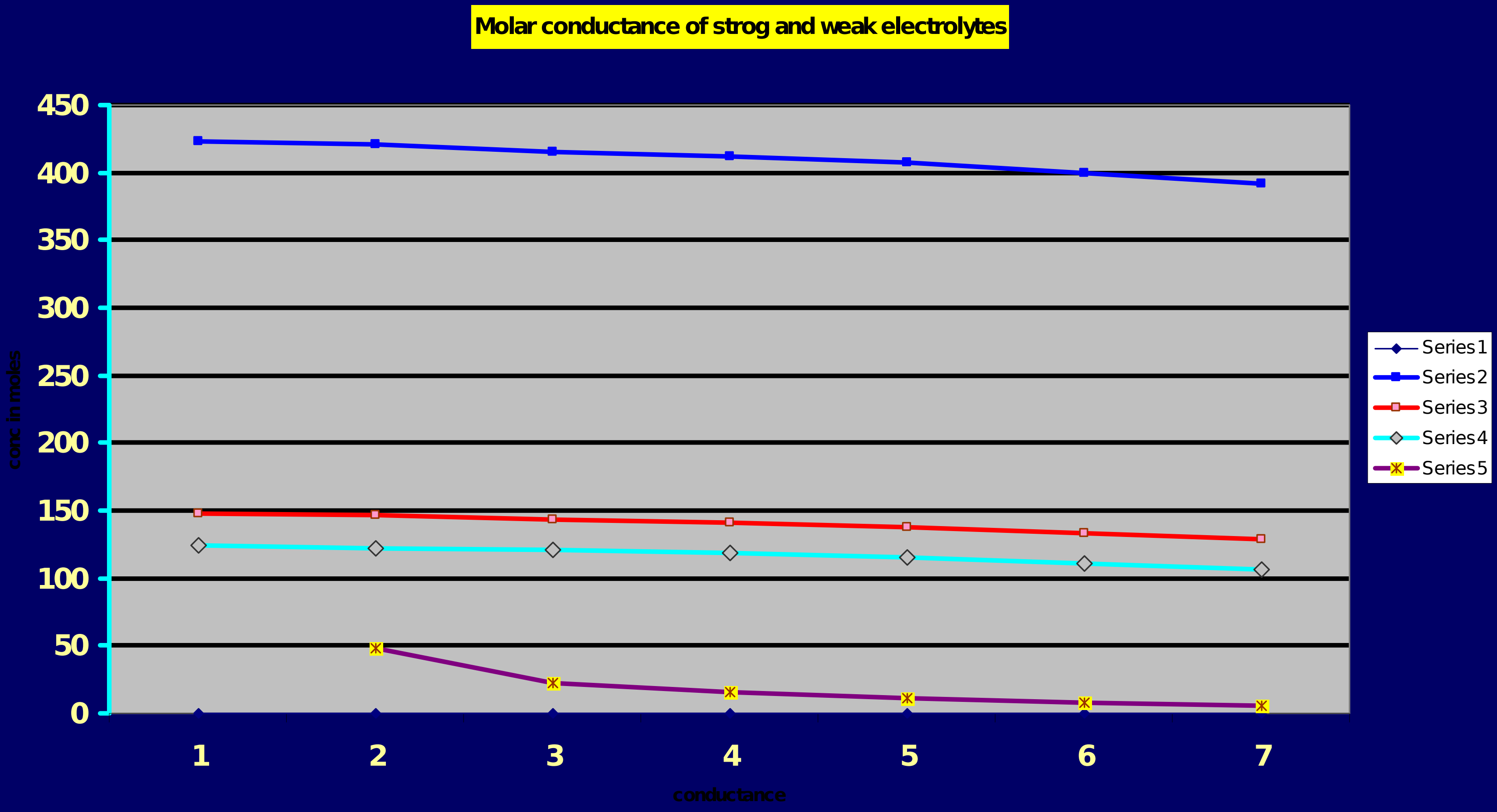


MOLAR CONDUCTIVITIES OF AQUEOUS SOLUTIONS AT 25°C

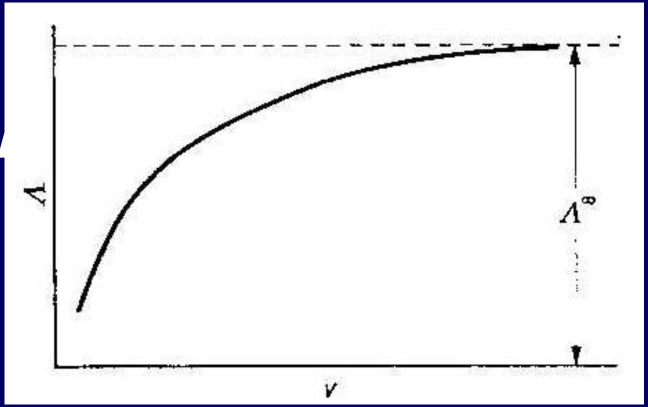
Concentration mol dm^{-3}	*Electrolyte* HCl	KCl	NaCl	$AgNO_3$	$\frac{1}{2}ZnSO_4$	$\frac{1}{2}NiSO_4$	HAc
0·0005	422·7	147·8	124·5	131·4	121·4	118·7	
0·001	421·4	147·0	123·7	130·5	114·5	113·1	48·63
0·005	415·8	143·6	120·7	127·2	95·5	93·2	22·80
0·01	412·0	141·3	118·5	124·8	84·9	82·7	16·20
0·02	407·2	138·2	115·8	121·4	74·2	72·3	11·57
0·05	399·1	133·4	111·1	115·2	61·2	59·2	7·36
0·10	391·3	129·0	106·7	109·1	52·6	50·8	5·20

(After *Handbook of Chemistry and Physics*, 37th ed., Chemical Rubber Publ. Co., 1955)

Plot of data on the previous slide



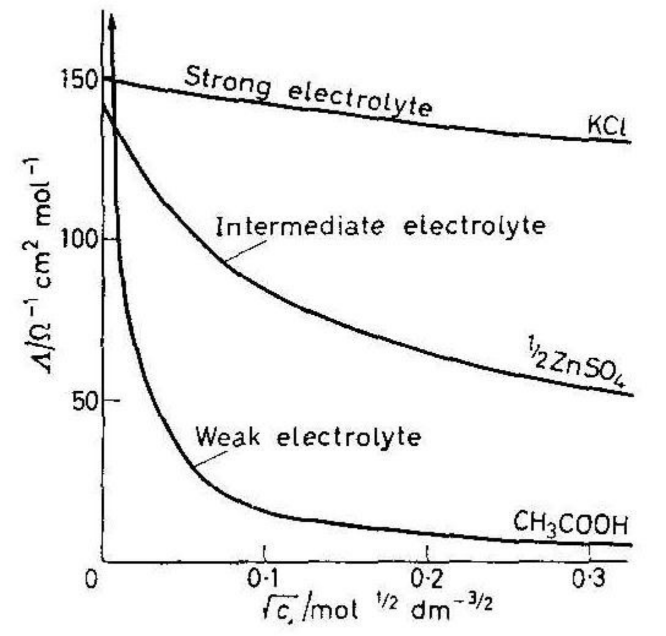
- These results show that, as the concentration decreases or the dilution increases, ***the molar conductivity increases and tends towards a limiting value which*** is known as the limiting molar conductivity and is denoted by the symbol Λ_∞. Thi generalized *in the fol*



$$\Lambda = \Lambda^{\infty} - k\sqrt{c}$$

- the relationship between molar conductivity, Λ, and concentration, c, could be expressed by the empirical equation : (k is a constant) This is the equation of a straight line of slope — k and intercept Λ^{∞}, and the relationship permits Λ^{∞} to be determined by extrapolation to zero concentration in those cases where the equation is applicable .

- The graph shows that there are two extremes of behaviour. Firstly, there are electrolytes, such as sodium and potassium chlorides, which exhibit fairly high values of molar conductivity over the whole concentration range considered. Such electrolytes are called *strong electrolytes.* Others show the behaviour exemplified by acetic acid. The molar conductivity remains low until very high dilutions are reached when it increases enormously. Such electrolytes are called *weak electrolytes*, and this class consists mostly of organic acids and bases. It is not always possible to draw a sharp distinction between strong and weak electrolytes, since the behaviour of some solutions, such as zinc sulphate, lies somewhere between the extremes. These are sometimes classed as *intermediate electrolytes*, of which some salts of the transition metals are the most important.



THEORIES OF IONISATTON

- Some attempts were made to explain ionization till 1887, when Arrhenius proposed his theory of ionization, that any degree of success was achieved.
- Arrhenius suggested that in a solution of an electrolyte, ions are always present in equilibrium with un-ionized molecules. Thus for a binary electrolyte, BA, there exists the equilibrium As the dilution increases, the equilibrium is displaced towards the right and more ionization occurs until, at infinite dilution, ionization is complete. Λ_∞ which is the limiting molar conductivity at infinite dilution should be a measure of the total number of ions which can be produced, and Λ at any other concentration C should be a measure of the of the number of ions present at C , then the ration of Λ to Λ_∞ will be equal to the degree of ionization

$$BA \rightleftharpoons B^+ + A^-$$

- Therefore the expression $\frac{\Lambda}{\Lambda^{\infty}} = \alpha$ should represent the magnitude o ionization. in other words α is the degree of ionization.
- Consider a binary electrolyte, BA, providing the ions B + and A- in solution where the concentration of BA is *c.* Suppose a fraction a of the BA ionizes so that the concentration of un-ionized BA is *c* (1 — a) and the concentr αc for each ion

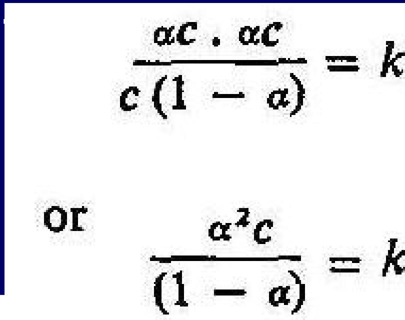
$$\begin{array}{cccc} \mathrm{BA} & \rightleftharpoons \mathrm{B}^{+} & + & \mathrm{A}^{-} \\ c\,(1-\alpha) & \alpha c & & \alpha c \end{array}$$

- The equilibrium law states that:

  where *k* is a constant

$$\frac{[\mathrm{B}^{+}]\,[\mathrm{A}^{-}]}{[\mathrm{BA}]} = k$$

- From the previous equation we can ge



$$\frac{\alpha c \,.\, \alpha c}{c\,(1-\alpha)} = k$$

or

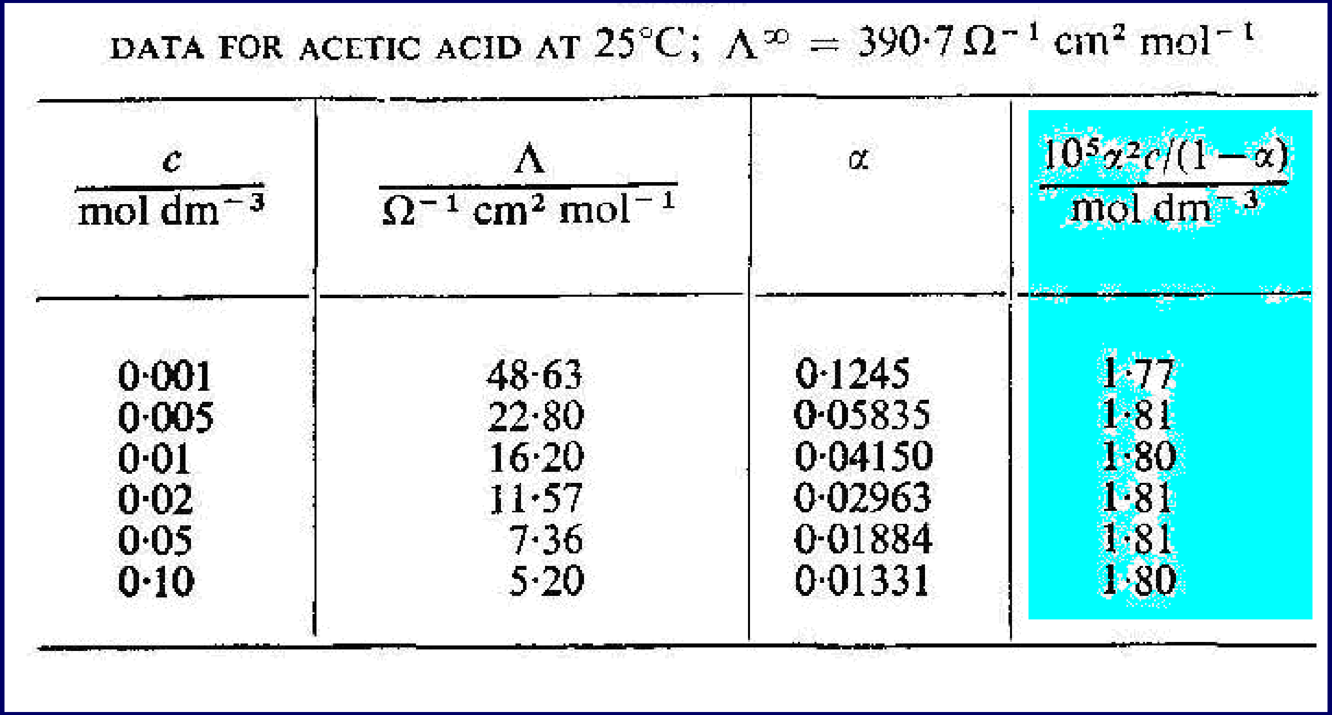
$$\frac{\alpha^2 c}{(1-\alpha)} = k$$

- The last equation is known as

Oswald's dilution law.

If the values of *α* derived from conductance measurements are correct, then substitution in the left-hand side of this equation should give a constant *.(Acetic acid is a weak electrolyte)*

(The equation Is correct)



DATA FOR ACETIC ACID AT 25°C; $\Lambda^{\infty} = 390{\cdot}7\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$

$\dfrac{c}{\mathrm{mol\ dm^{-3}}}$	$\dfrac{\Lambda}{\Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}}$	α	$\dfrac{10^5\alpha^2c/(1-\alpha)}{\mathrm{mol\ dm^{-3}}}$
0·001	48·63	0·1245	1·77
0·005	22·80	0·05835	1·81
0·01	16·20	0·04150	1·80
0·02	11·57	0·02963	1·81
0·05	7·36	0·01884	1·81
0·10	5·20	0·01331	1·80

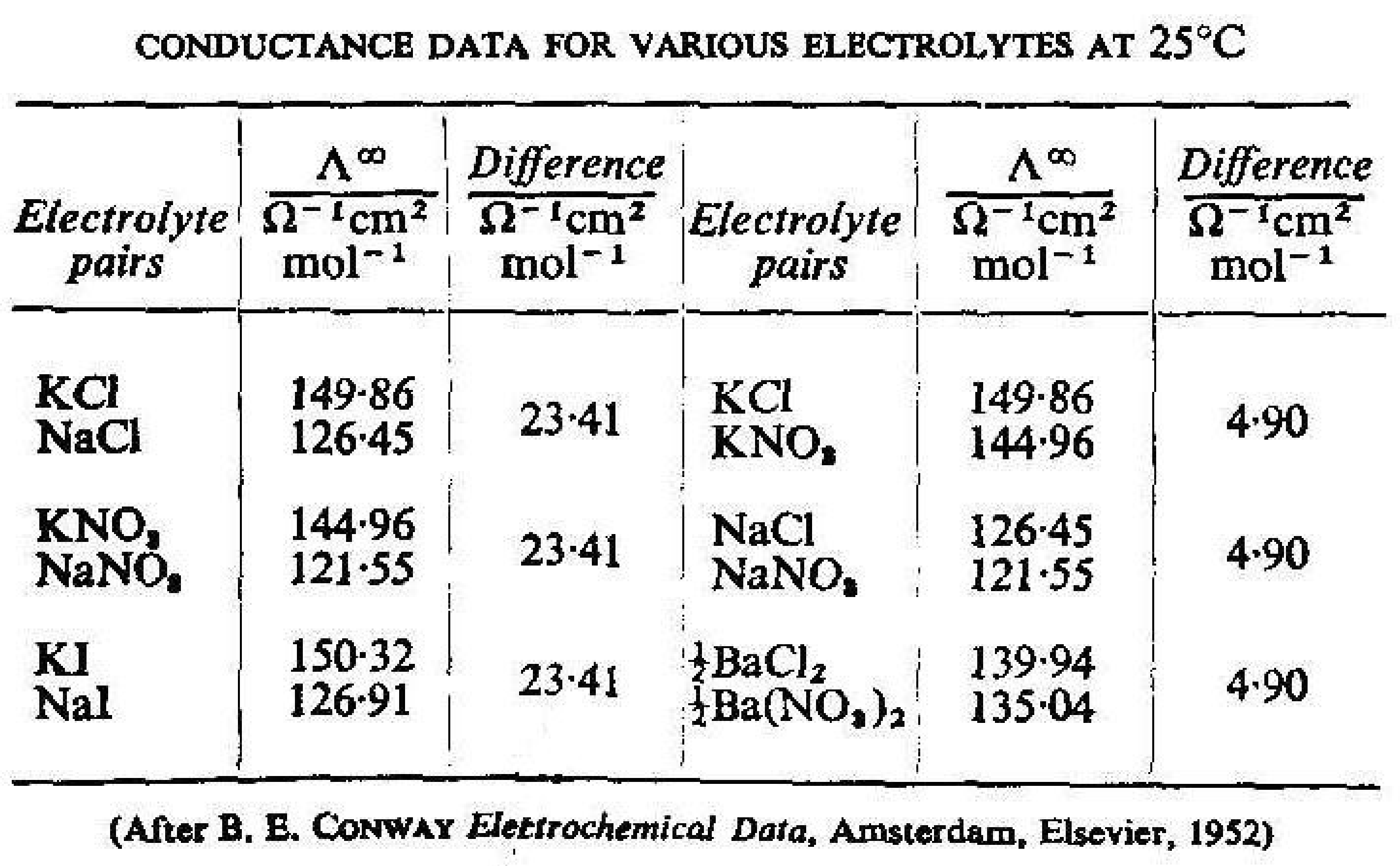
What about if the electrolyte is strong?

- Data for strong electrolytes, such as that given for potassium chloride below, show that the theory fails in their case. The only conclusion to be drawn is that, for strong electrolytes, Λ/Λ_∞ is not equal to the degree of ionization.
- The conductance of a strong electrolyte which is completely dissociated in solution, for example, sodium chloride , here the sodium ions and chloride ions will not be distributed randomly throughout the solvent. Each sodium ion, being positively charged, will attract towards itself the negatively charged chloride ions and tend to repel other sodium ions. These electrostatic forces will he offset to a large extent by the thermal motion of the ions, but on balance every sodium ion will be surrounded by an ion cloud containing more chloride than sodium ions. Conversely, each chloride ion will have its ion cloud containing more sodium than chloride ions.

- When the current flows, the sodium ion will move towards the cathode and its ion cloud will move in the opposite direction. The original ion cloud will break up and a new one will form. In practice, a short time is required for the completion of this operation, and this is known as the *time of relaxation.* Thus, before the original ion cloud has decayed, the sodium ion will be off centre and there will be a net backward attraction. The speed of the sodium ion will thus be reduced. This effect is called the *relaxation effect* or the *asymmetry effect.*

  As the solution is diluted, the ions are spread out farther apart and the density of the ion cloud decreases. Hence the interionic attraction forces are less and the speed of the ion increases. consequently, charge is being transferred at a greater rate, thus giving rise to a greater current, and the molar conductivity of the solution increases. This change will continue until, at infinite dilution, the ions are an infinite distance apart and interionic effects are zero. Under these conditions, i.e. at infinite dilution, the molar conductivity will be a maximum.

LIMITING MOLAR CONDUCTIVITIES OF IONS STOP



CONDUCTANCE DATA FOR VARIOUS ELECTROLYTES AT 25°C

Electrolyte pairs	Λ^∞ $\Omega^{-1}cm^2\,mol^{-1}$	*Difference* $\Omega^{-1}cm^2\,mol^{-1}$	*Electrolyte pairs*	Λ^∞ $\Omega^{-1}cm^2\,mol^{-1}$	*Difference* $\Omega^{-1}cm^2\,mol^{-1}$
KCl	149·86	23·41	KCl	149·86	4·90
NaCl	126·45		KNO_3	144·96	
KNO_3	144·96	23·41	NaCl	126·45	4·90
$NaNO_3$	121·55		$NaNO_3$	121·55	
KI	150·32	23·41	$\frac{1}{2}BaCl_2$	139·94	4·90
NaI	126·91		$\frac{1}{2}Ba(NO_3)_2$	135·04	

(After B. E. CONWAY *Electrochemical Data*, Amsterdam, Elsevier, 1952)

- The previous table gives us indication about the resistivity and quantity of charge carried by different ions.

Ag 1 mol; Cu ½ mol; Cr 1/3

The cathode processes are:

$Ag_{(aq)} + e^- \rightarrow Ag_{(s)}$

$Cu^{+2} + 2e^- \rightarrow Cu_{(s)}$

$Cr^{+3} + 3e- \rightarrow Cr_{(s)}$

We can construct a table similar to this:

Element	**Electrochemical equivalent** **SEE NEXT SLIDE**	**Q/C** **Equivalent weight**	**Valency**
Hydrogen	**1.045×10^{-5}**	**1.008**	**1**
Silver	**1.118×10^{-5}**	**107.9**	**1**
Oxygen	**8.29×10^{-5}**	**16.0**	**2**
Copper	**3.29×10^{-5}**	**63.5**	**2**
Chromium	**1.80×10^{-5}**	**28.9**	**3**

What is the electrochemical equivalent?

- The electrochemical equivalent of a substance is equal to the gram-atomic or gram-molecular mass of this substance divided by the number of electrons involved in the electrode reaction. For example, the electrochemical equivalent of zinc, for which two electrons are required in order to deposit one atom, is Zn/2 or 65.37/2 g. Thus, the faraday is equal to the product of the charge of the electron times the number of electrons required to react with 1 atom- or molecule-equivalent of substance.

Faraday Laws of Electrolysis

Faraday's laws of ***electrolysis*** are quantitative relationships based on the electrochemical researches published by Michael ***Faraday*** in 1834

- The amount of primary product formed at an electrode by electrolysis is directly proportional to the quantity of electricity passed.
- The amounts of various primary products formed at an electrode by the same quantity of electricity are proportional to their relative masses divided by the change in their charge numbers for the electrode process.
- The third law is a consequence of 1+2 which can be summarized as: You need one Faraday to deposit of evolve one equivalent of a metal (SEE NEXT SLIDE)

- Faraday's laws can be summarized by
- Where

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right)$$

  - m is the mass of the substance altered at an electrode
  - Q is the total electric charge passed through the substance
  - F = 96,485 C mol-1 is the Faraday constant
  - M is the molar mass of the substance
  - z is the valency number of ions of the substance (electrons transferred per ion)
- Note that M / z is the same as the equivalent weight of the substance altered.

Explanations

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right)$$

- For Faraday's ***first law***, *M*, *F*, and *z* are constants, so that the larger the value of *Q* the larger m will be.
- For Faraday's ***second law***, *Q*, *F*, and *z* are constants, so that the larger the value of *M / z* (equivalent weight) the larger m will be.
- In the simple case of constant-current electrolysis, $Q = It$ leading to
  - $$m = \left(\frac{It}{F}\right)\left(\frac{M}{z}\right)$$
- and then to
  - $$n = \left(\frac{It}{F}\right)\left(\frac{1}{z}\right)$$
- where
  - *n* is the amount of substance ("number of moles") altered: $n = m / M$
  - *t* is the total time the constant current was applied.

REMEMBER THAT:

A Faraday (*F*) is the amount of electricity that reduces one equivalent of a species at the cathode and oxidizes one equivalent of a species at the anode.

$$1\ \text{faraday} \equiv 6.022 \times 10^{23}\ e^{-} \equiv 96{,}487\ \text{coulombs}$$

Counting Electrons: Coulometry and Faraday’ Law of Electrolysis

- Faraday’s Law states that during electrolysis, one faraday of electricity (96,487 coulombs) reduces and oxidizes, respectively, one equivalent of the oxidizing agent and the reducing agent.
  - This corresponds to the passage of one mole of electrons through the electrolytic cell.

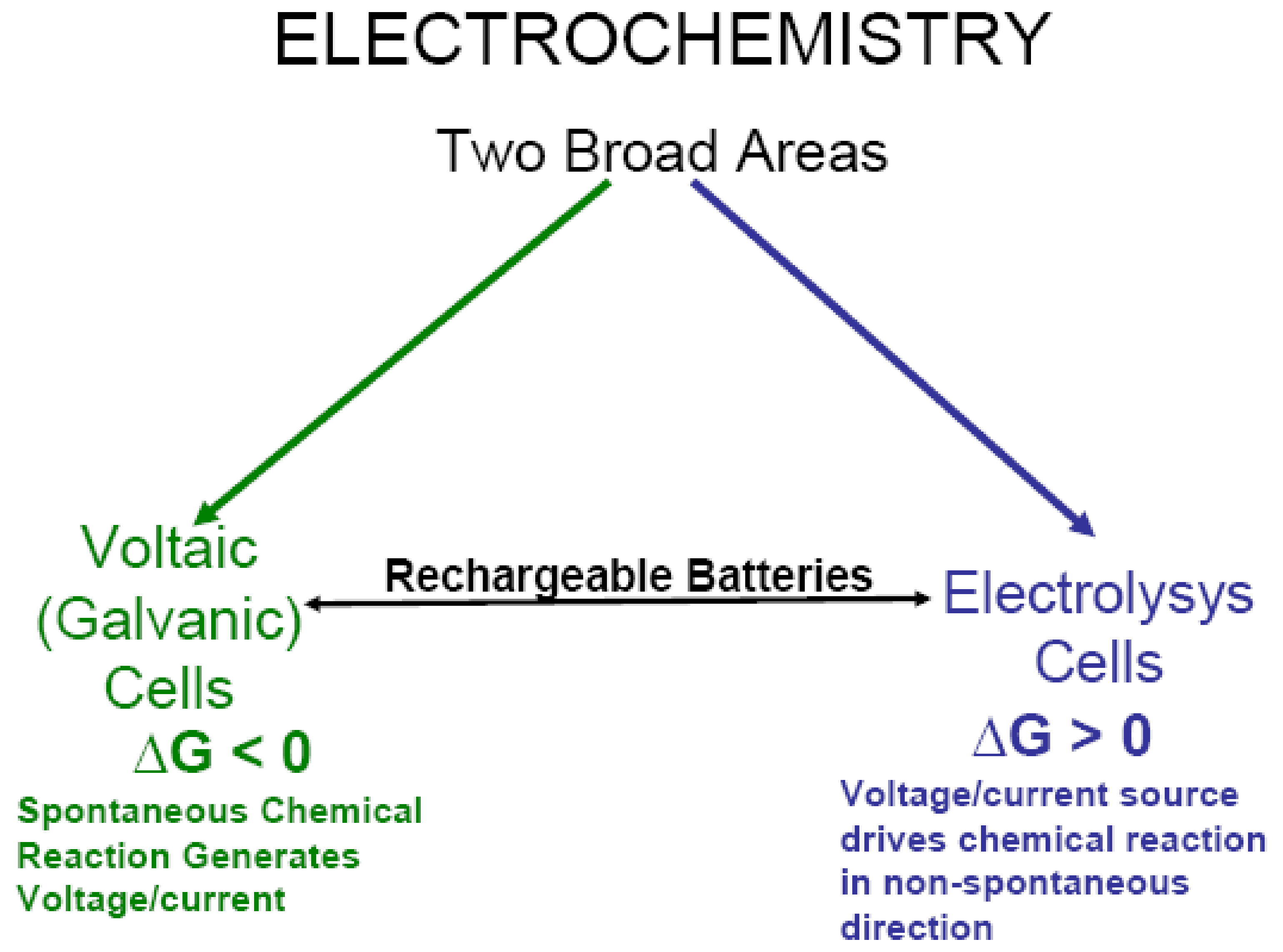
$$1\ \text{equivalent of oxidizing agent} \equiv \text{gain of } 6.022\times10^{23}\ e^{-}$$

$$1\ \text{equivalent of reducing agent} \equiv \text{loss of } 6.022\times10^{23}\ e^{-}$$

Electrochemistry

- Electrochemical reactions are oxidation-reduction reactions.
- The two parts of the reaction are physically separated.
  - The oxidation reaction occurs in one cell.
  - The reduction reaction occurs in the other cell.
- There are two kinds electrochemical cells.

1. Electrochemical cells containing in nonspontaneous chemical reactions are called **electrolytic cells**.
2. Electrochemical cells containing spontaneous chemical reactions are called **voltaic** or **galvanic cells**.



ELECTROCHEMISTRY

Two Broad Areas

Voltaic (Galvanic) Cells

$\Delta G < 0$

Spontaneous Chemical Reaction Generates Voltage/current

Rechargeable Batteries

Electrolysys Cells

$\Delta G > 0$

Voltage/current source drives chemical reaction in non-spontaneous direction

Electrolytic Cells

- **Electrical energy** is used to force nonspontaneous chemical reactions to occur.
- The process is called electrolysis.
- Two examples of commercial electrolytic reactions are:

1. The electroplating of jewelry and auto parts.
2. The electrolysis of chemical compounds.

The Electrolysis of Molten Potassium Chloride

- Liquid potassium is produced at one electrode.
  - Indicates that the reaction $K^+(\ell) + e^- \rightarrow K(\ell)$ occurs at this electrode. (TAKES PLACE AT THE CATHODE)
- Gaseous chlorine is produced at the other electrode.
  - Indicates that the reaction $2\ Cl^- \rightarrow Cl_2(g) + 2\ e^-$ occurs at this electrode. (TAKES PLACE AT THE ANODE)

The Electrolysis of Molten Potassium Chloride

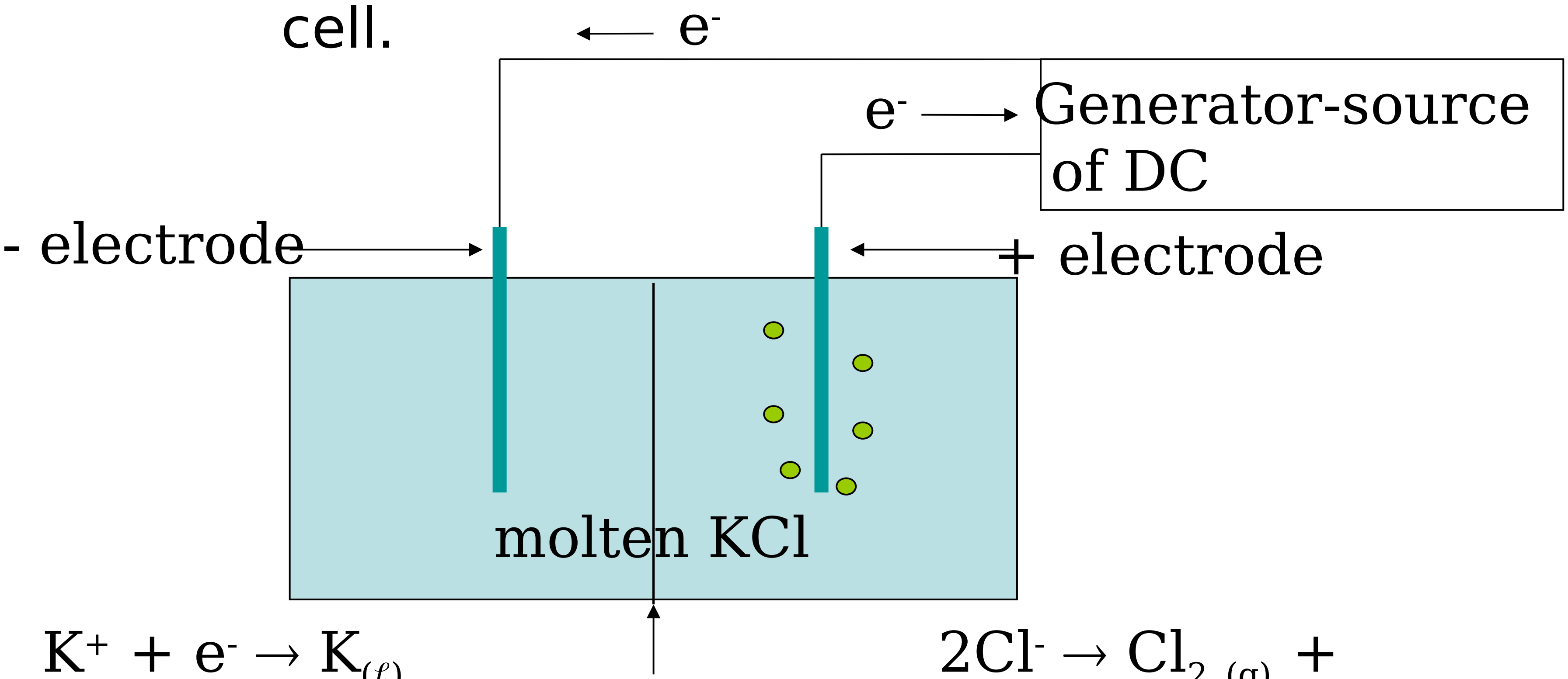
- The **nonspontaneous** redox reaction that occurs is:

$$\begin{array}{ll} \text{Anode reaction} & 2\,\mathrm{Cl}^- \rightarrow \mathrm{Cl}_{2(g)} + 2\,e^- \\ \underline{\text{Cathode reaction}} & \underline{2\left(\mathrm{K}^+ + e^- \rightarrow \mathrm{K}_{(\ell)}\right)} \\ \text{Cell reaction} & 2\,\mathrm{Cl}^- + 2\,\mathrm{K}^+ \rightarrow \mathrm{Cl}_{2(g)} + 2\,\mathrm{K}_{(\ell)} \end{array}$$

- In all **electrolytic cells**, electrons are **forced** to flow from the **positive electrode (anode)** to the **negative electrode (cathode)**.

The Electrolysis of Molten Potassium Chloride

Diagram of this electrolytic cell.



e^-

e^-

Generator-source of DC

- electrode

+ electrode

molten KCl

Porous barrier

$K^+ + e^- \rightarrow K_{(\ell)}$

cathode reaction

$2Cl^- \rightarrow Cl_{2\ (g)} + 2e^-$

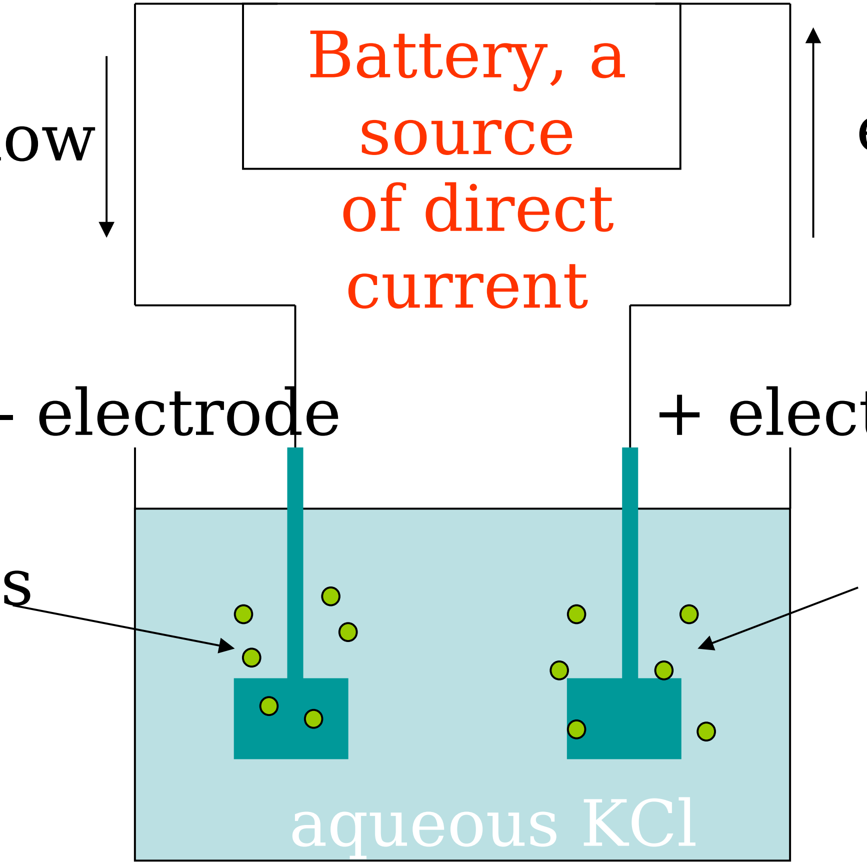
anode reaction

The Electrolysis of Aqueous Potassium Chloride

- In this electrolytic cell, hydrogen gas is produced at one electrode.(see next slide for reactions)
  - The aqueous solution becomes basic near this electrode.
  - What reaction is occurring at this electrode? ***You do it!***
- Gaseous chlorine is produced at the other electrode.
  - What reaction is occurring at this electrode? ***You do it!***
- These experimental facts lead us to the following nonspontaneous electrode reactions:

The Electrolysis of Aqueous Potassium Chloride

Cell diagram



- pole of battery

+ pole of battery

e^- flow

Battery, a source of direct current

e^- flow

- electrode

+ electrode

H_2 gas

Cl_2 gas

aqueous KCl

$2\ H_2O + 2e^- \rightarrow H_{2\ (g)} + 2\ OH^-$

$2Cl^- \rightarrow Cl_{2\ (g)} + 2e^-$

The Electrolysis of Aqueous Potassium Sulfate

- In this electrolysis, hydrogen gas is produced at one electrode.
  - The solution becomes basic near this electrode.
  - What reaction is occurring at this electrode?

You do it!

- Gaseous oxygen is produced at the other electrode
  - The solution becomes acidic near this electrode.
  - What reaction is occurring at this electrode?

You do it!

- These experimental facts lead us to the following electrode reactions:

The Electrolysis of Aqueous Potassium Sulfate

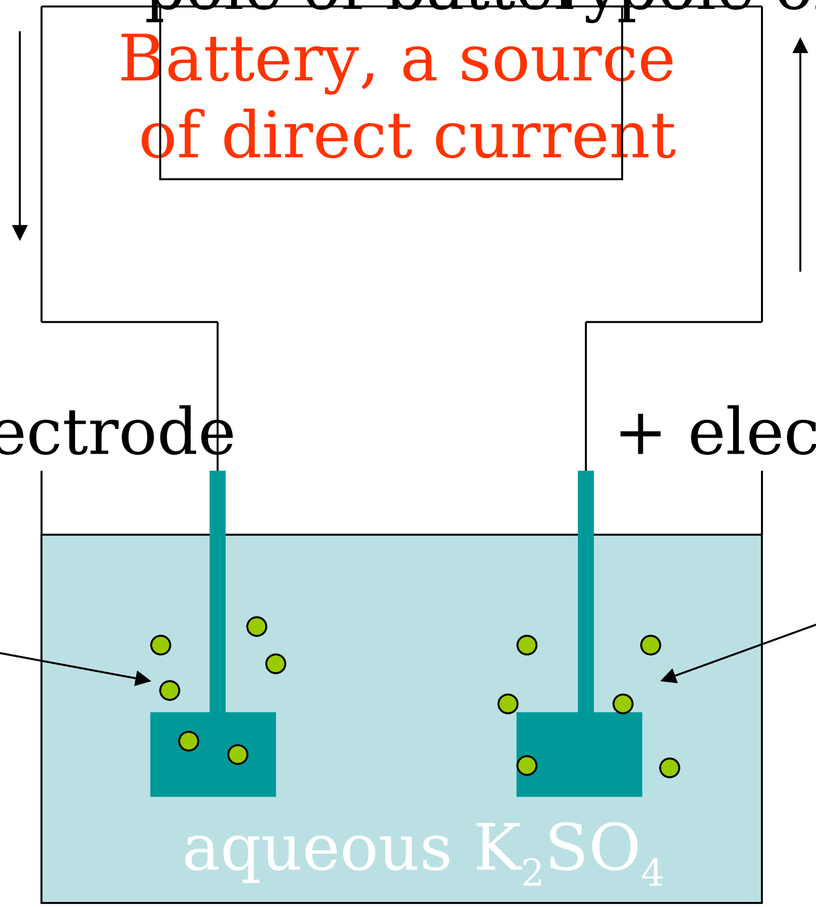
Anode reaction $2H_2O \rightarrow O_{2(g)} + 4H^+ + 4e^-$

Cathode reaction $2(2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-)$

Cell reaction $6H_2O \rightarrow 2H_{2(g)} + O_{2(g)} + \underbrace{4H^+ + 4OH^-}_{4H_2O}$

The overall reaction is $2H_2O \rightarrow 2H_{2(g)} + O_{2(g)}$

The Electrolysis of Aqueous Potassium Sulfate



Cell diagram

- pole of battery

+ pole of battery

Battery, a source of direct current

e^- flow

e^- flow

- electrode

+ electrode

H_2 gas

O_2 gas

aqueous K_2SO_4

$2\ H_2O + 2e^- \rightarrow H_{2\ (g)} + 2\ OH^-$

$2H_2O \rightarrow O_{2\ (g)} + 4H^+ + 4e^-$

Electrolytic Cells

- In all electrolytic cells the most easily reduced species is reduced and the most easily oxidized species is oxidized.

Calculations

- Example -1: Calculate the mass of palladium produced by the reduction of palladium (II) ions during the passage of 3.20 amperes of current through a solution of palladium (II) sulfate for 30.0 minutes. (Atomic mass for Pd is 106,

$$\begin{array}{lccccc} \text{Cathode:} & Pd^{2+} & + & 2e^{-} & \rightarrow & Pd^{0} \\ & 1\text{ mol} & & 2\text{ mol} & & 1\text{ mol} \\ & 106\text{ g} & & 2(96{,}500) & & 106\text{ g} \end{array}$$

$$3.20\text{ amp} = 3.20\ {}^{C}\!/\!_{s}$$

$$?\text{ g} = 30.0\text{ min} \times \frac{60\text{ s}}{\text{min}} \times \frac{3.20\text{ C}}{\text{s}} \times \frac{106\text{ g Pd}}{2(96{,}500\text{ C})} = 3.16\text{ g Pd}$$

- Example -2: Calculate the volume of oxygen (measured at STP) produced by the oxidation of water in the previous *example 1*.

$$\begin{array}{lcccc} \text{Anode}: 2\,H_2O \rightarrow & O_{2(g)} & +4H^+ & +4e^- \\ 2\,\text{mol} & 1\,\text{mol} & 4\,\text{mol} & 4\,\text{mol} \\ & 22.4\,L_{STP} & & 4(96{,}500\,C) \end{array}$$

$$?\,L_{STP}\;O_2 = 30.0\,\text{min} \times \frac{60\,\text{s}}{\text{min}} \times \frac{3.20\,C}{\text{s}} \times \frac{22.4\,L_{STP}\;O_2}{4(96{,}500\,C)}$$

$$= 0.334\,L_{STP}\;O_2 \text{ or } 334\,mL_{STP}\;O_2$$

Commercial Applications of Electrolytic Cells

Electrolytic Refining and Electroplating of Metals

- Impure metallic copper can be purified electrolytically to ≈ 100% pure Cu.
  - The impurities commonly include some active metals plus less active metals such as: Ag, Au, and Pt.
- The cathode is a thin sheet of copper metal connected to the negative terminal of a direct current source.
- The anode is large impure bars of copper.

Commercial Applications of Electrolytic Cells

- The electrolytic solution is $CuSO_4$ and H_2SO_4
- The impure Cu dissolves to form Cu^{2+}.
- The Cu^{2+} ions are reduced to Cu at the cathode.

$$\text{Anode impure} \quad Cu^{0}_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^{-}$$

$$\text{Cathode very pure} \quad Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu^{0}_{(s)}$$

Net rxn. No net rxn.

Voltaic or Galvanic Cells

- Electrochemical cells in which a spontaneous chemical reaction produces electrical energy.
- Cell halves are physically separated so that electrons (from redox reaction) are forced to travel through wires and creating a potential difference.
- Examples of voltaic cells include:

Auto batteries

Flashlight batteries

Computer and calculator batteries

The Construction of Simple Voltaic Cells

- Voltaic cells consist of two half-cells which contain the oxidized and reduced forms of an element (or other chemical species) in contact with each other.
- A simple half-cell consists of:
  - A piece of metal immersed in a solution of its ions.
  - A wire to connect the two half-cells.
  - And a salt bridge to complete the circuit, maintain neutrality, and prevent solution mixing.

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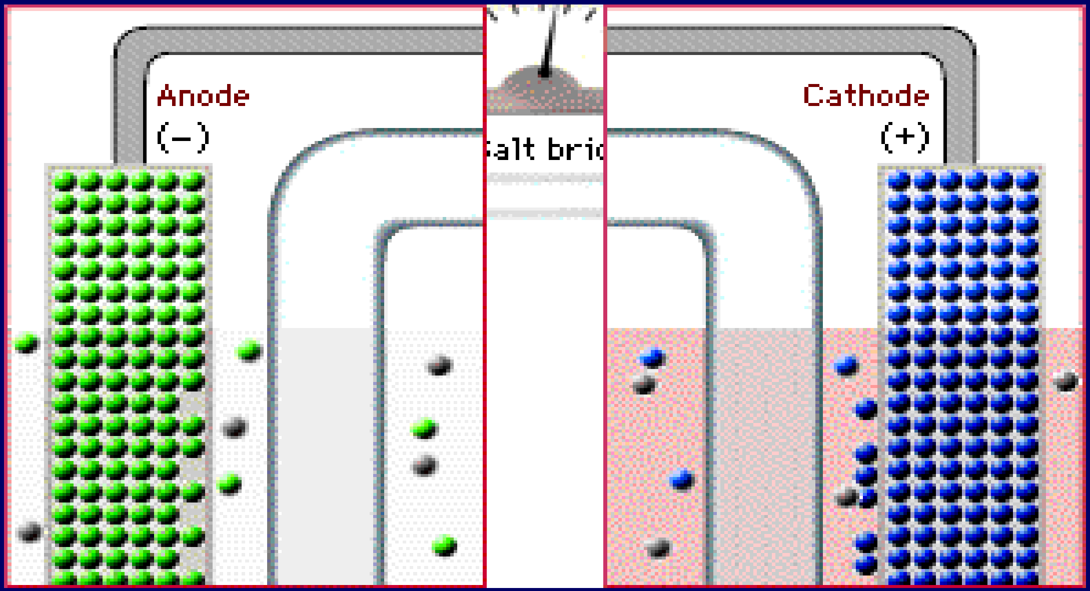
The Construction of Simple Voltaic Cells



The Zinc-Copper Cell

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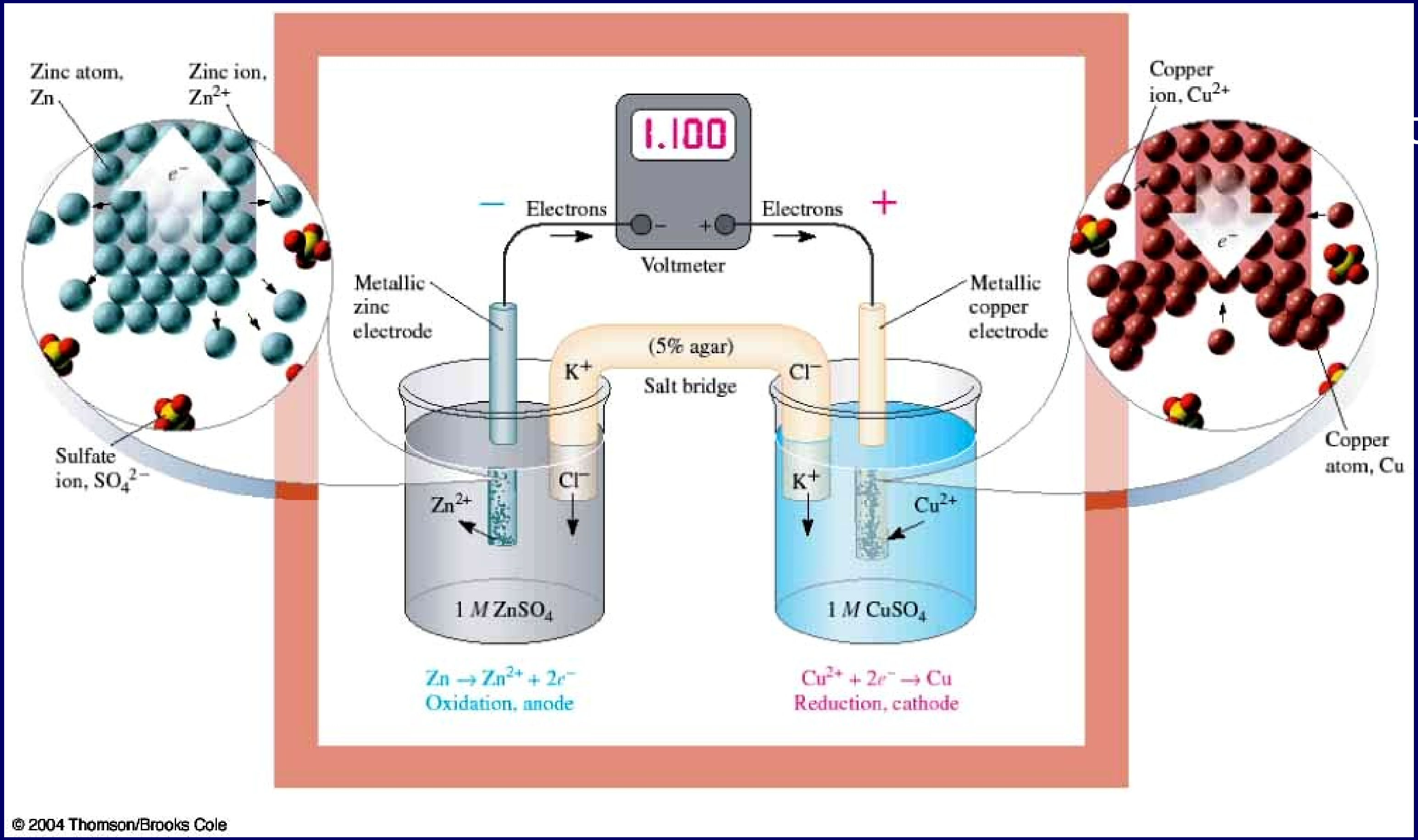

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The Zinc-Copper Cell

$$\text{Anode reaction} \qquad Zn^0 \rightarrow Zn^{2+} + 2e^-$$

$$\underline{\text{Cathode reaction} \qquad Cu^{2+} + 2e^- \rightarrow Cu^0}$$

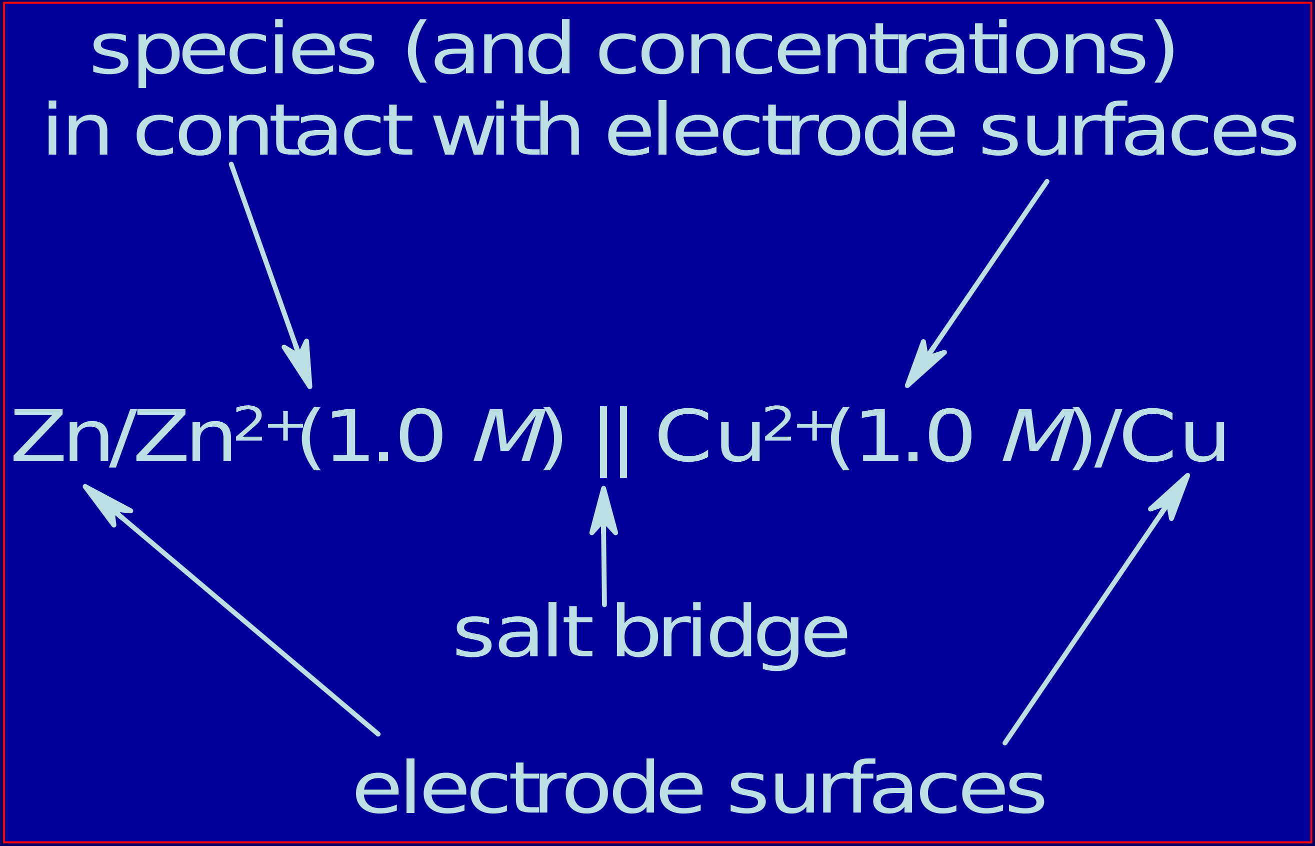
$$\text{Overall cell reaction} \quad Zn^0 + Cu^{2+} \rightarrow Zn^{2+} + Cu^0$$

$$\text{This is a spontaneous reaction with } E^0_{cell} = +1.10V$$

- **In all voltaic cells, electrons flow spontaneously from the negative electrode (anode) to the positive electrode (cathode).**

The Zinc-Copper Cell

- There is a commonly used short hand notation for voltaic cells.
  - The Zn-Cu cell provides a good example.



species (and concentrations) in contact with electrode surfaces

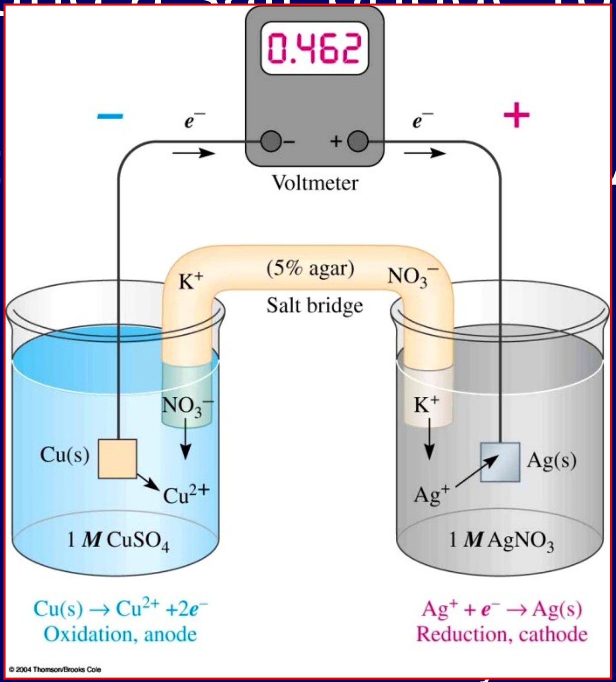
$\mathrm{Zn}/\mathrm{Zn}^{2+}(1.0\ M)\ ||\ \mathrm{Cu}^{2+}(1.0\ M)/\mathrm{Cu}$

salt bridge

electrode surfaces

The Copper - Silver Cell

- Cell components:
  1. A Cu strip immersed in 1.0 *M* copper (II) sulfate.
  2. A Ag strip immersed in 1.0 *M* silver (I) nitrate.
  3. A wire and a salt bridge to complete the circuit.
- The initial c volts.



The Copper - Silver Cell

Anode reaction $\quad Cu^0 \rightarrow Cu^{2+} + 2e^-$

Cathode reaction $\quad 2\left(Ag^+ + e^- \rightarrow Ag^0\right)$

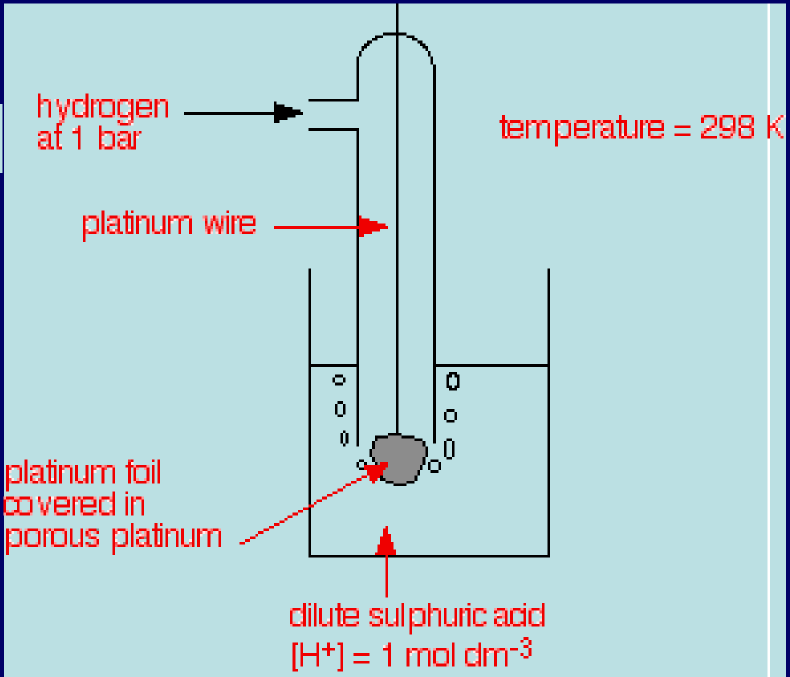
Overall cell reaction $\quad Cu^0 + 2Ag^+ \rightarrow Cu^{2+} + 2Ag^0$

This is a spontaneous reaction with $E^0_{cell} = +0.46V$

- Compare the Zn-Cu cell to the Cu-Ag cell
  - The Cu electrode is the cathode in the Zn-Cu cell.
  - The Cu electrode is the anode in the Cu-Ag cell.
- Whether a particular electrode behaves as an anode or as a cathode depends on what the other electrode of the cell is.

- **The standard hydrogen electrode**
- The standard hydrogen electrode looks like this:
- As the hydrogen gas flows over the porous platinum, an equilibrium is set up between hydrogen molecules and hydrogen ions in solution. The reaction is catalysed by the platinum.

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$$



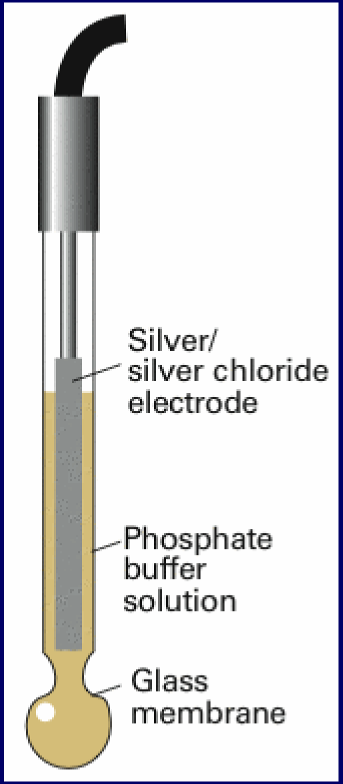
Applications of standard potentials
a-Species-selective electrodes

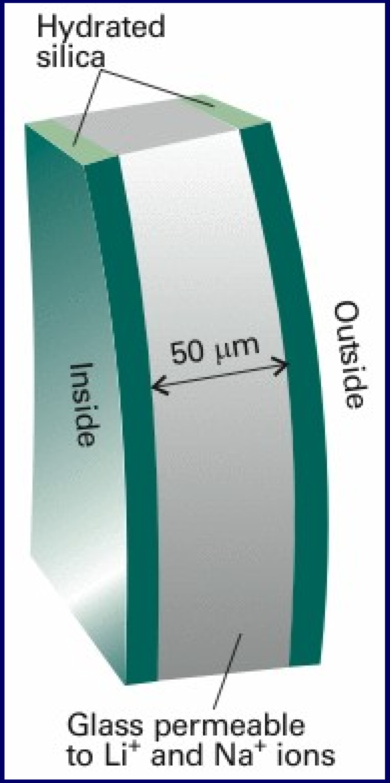
- The glass electrode.

It is commonly used in conjunction with a calomel electrode that makes contact with the test solution through a salt bridge.

We can design “selective electrodes for most metals and non-metals.

Thus their concentrations can be measured irrespective what other ions are present.



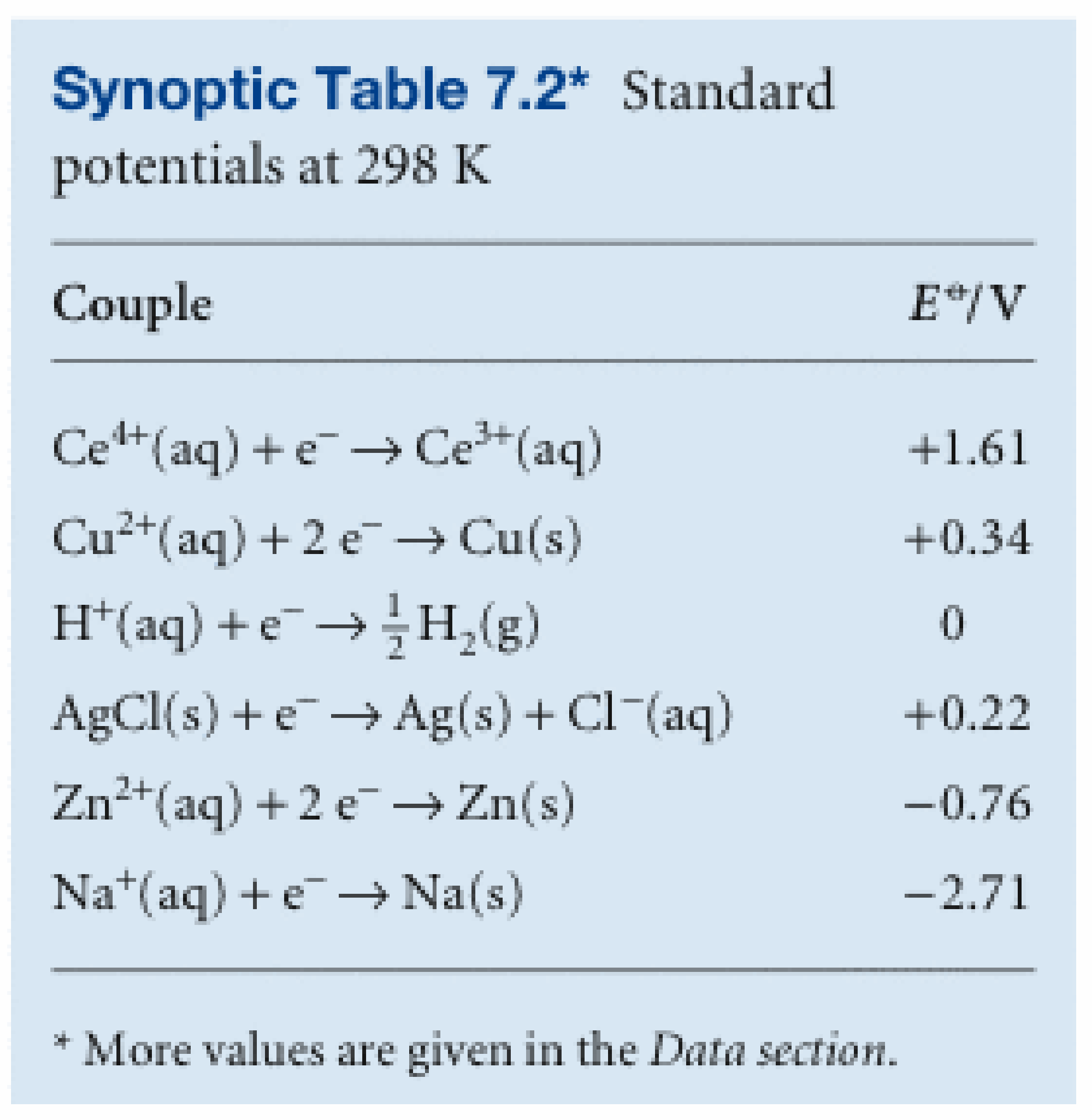


Standard conditions for measuring potential differences

- The position of any equilibrium can be changed by changing conditions. That means that the conditions must be standardized so that you can make fair comparisons.
- The hydrogen pressure is 1 bar (100 kPa).
- The temperature is 298 K (25°C).
- The concentration of the hydrogen ions in solution is also important. Changing concentrations is one of the ways of changing the position of an equilibrium. Throughout this topic, all ions concentrations are taken as being 1 mol dm^{-3}.

- To achieve the standard conditions, the activity of the hydrogen ions must be 1 (that is, pH = 0) and the pressure must be 1 bar. The **standard potential**, *E*, of another couple is then assigned by constructing a cell in which it is the right-hand electrode and the standard hydrogen electrode is the left-hand electrode.
- The procedure for measuring a standard potential can be illustrated by considering a specific case, the silver chloride electrode. The measurement is made on the 'Harned cell':

$\mathrm{Pt(s)|H_2(g)|HCl(aq)|AgCl(s)|Ag(s)}$ $\quad$ $\frac{1}{2}\mathrm{H_2(g) + AgCl(s) \rightarrow HCl(aq) + Ag(s)}$



Synoptic Table 7.2* Standard potentials at 298 K

Couple	$E^\ominus$/V
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$	+0.34
$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$	0
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	−0.76
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71

* More values are given in the *Data section*.

The electrochemical series

- From standard potentials,
- we can arrange metals
- according to these values
- as seen here:

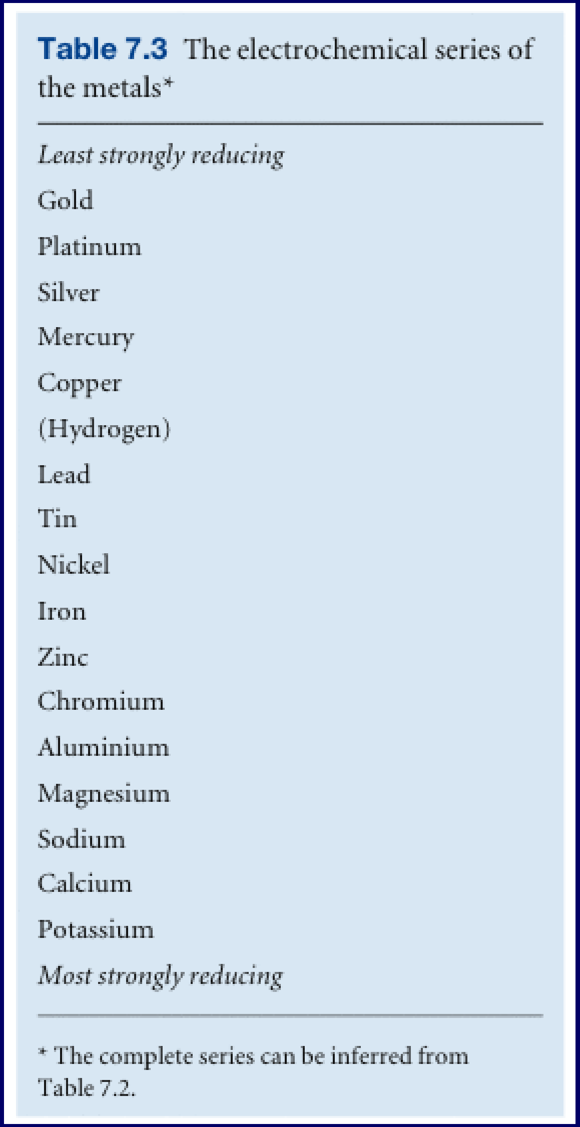


Table 7.3 The electrochemical series of the metals*

Least strongly reducing

Gold

Platinum

Silver

Mercury

Copper

(Hydrogen)

Lead

Tin

Nickel

Iron

Zinc

Chromium

Aluminium

Magnesium

Sodium

Calcium

Potassium

Most strongly reducing

---

* The complete series can be inferred from Table 7.2.